clopentenone annulation at an olefinic linkage.

The present methodology for C-carbonylation of a carbonyl compound (i.e., the use of Lewis-acidic silicon to bind unshared electrons of the carbonyl oxygen) could be broader than mononuclear catalyst system. A cluster or a heterogenous surface, having a metal center and a Lewis-acid center located at a suitable distance, might also be envisaged as a potentially effective catalyst.

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Supplementary Material Available: Characterization of new products and a literature survey of synthetic transformations via disiloxyalkenes (8 pages). Ordering information is given on any current masthead page.

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(19) A mixture of **11** (0.5 mmol, 0.20 g) and 60% phosphoric acid (2.3 mL) was heated at 90 °C for 5 h, extracted with benzene, and dried. Chromatography (silica gel, *n*-hexane/Et_2O = 8/2) gave **12** (61 mg, 66%). Cf.: Hirano, S.; Takagi, S.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 169.

Synthesis of Neutral Ruthenium Formyls by Hydride Transfer from $[Ph_3PCuH]_6$. Evidence for a Radical-Initiated Decomposition of Neutral Formyl Complexes

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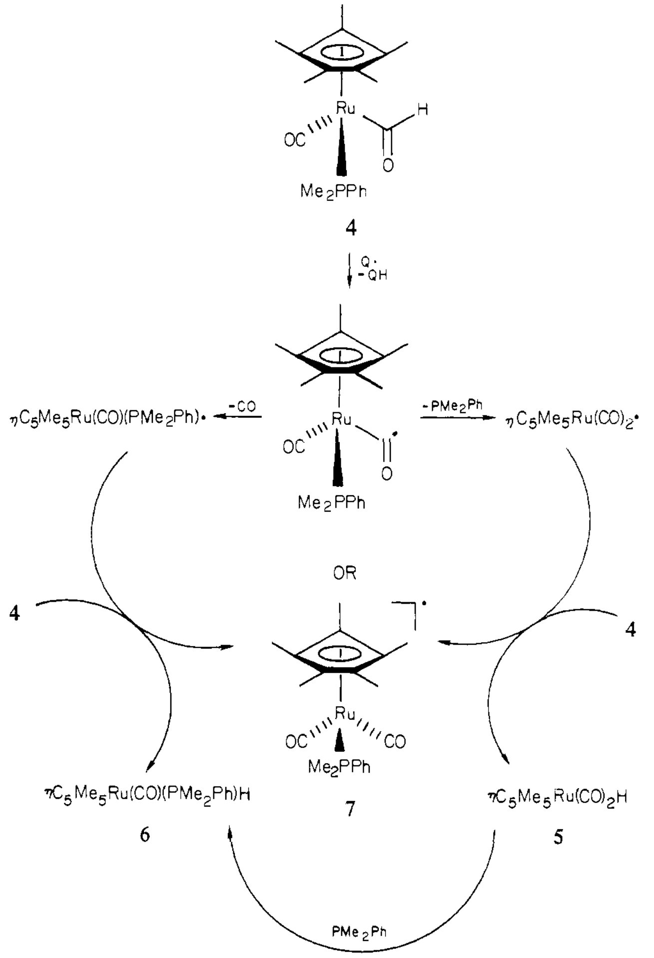
In recent years increased importance has been placed on the understanding of mechanistic routes involved in the reduction of carbon monoxide by transition-metal complexes.[1] During the course of these studies, metal formyl and metal hydroxyalkyl complexes have been proposed as viable intermediates in the reduction of carbon monoxide.[1,2] We report here the reaction of a transition-metal hydride cluster, $[Ph_3PCuH]_6$,[3] with $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$ (**1**)[4] and $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (**2**) to produce the new neutral formyl complexes $(\eta\text{-}C_5Me_5)Ru(CO)_2CHO$ (**3**) and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$ (**4**).[5] In addition, we disclose data that indicate that neutral formyl complexes can decompose by a radical chain mechanism and are, therefore, stabilized in the presence of radical scavengers.

Scheme I



When 1 equiv of red $[Ph_3PCuH]_6$[3] (238 mg, 0.12 mmol) dissolved in 2 mL of degassed THF (tetrahydrofuran) is added to a THF (2 mL) slurry of $(\eta\text{-}C_5Me_5)Ru(CO)_3{}^+BF_4{}^-$[4] (50 mg, 0.12 mmol), the resulting solution almost immediately turns pale yellow with concomitant precipitation of a yellow, copper-containing solid. IR and ^1H NMR show that this solution contains approximately a 1:1 mixture of $(\eta\text{-}C_5Me_5)Ru(CO)_2H$ (**5**) and $(\eta\text{-}C_5Me_5)Ru(CO)_2CHO$ (**3**). The hydride complex **5** is known,[4] and **3** is clearly identified by its carbonyl stretches [γ_{CO} (THF) = 2020, 1965, 1642 cm^{-1}] and its ^1H NMR (C_6D_6), which shows singlets at δ 14.0 (CHO) and 1.50 (C_5Me_5). Interestingly, **3** shows varying degrees of stability, which range from decomposing rapidly to **5** to persisting for several hours. This behavior is reminiscent of radical-initiated organometallic reactions,[6] and in fact, the presence of radical scavengers causes a marked change in the copper hydride reduction just described. When the reduction is performed in the presence of 5 equiv of 9,10-dihydroanthracene, a known hydrogen atom donor,[7] the formyl complex is quantitatively formed by IR and NMR. Complex **3** still decomposes over several hours, and attempts to isolate it always give a mixture of **3** and **5**. Extremely brief exposure of **3** to air causes the complete transformation of **3** to **5**.

A deeper probe of the radical character of the decomposition of neutral formyl complexes is possible with the stable phosphine-substituted complex $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)CHO$ (**4**). Although **4** can be synthesized from cation **2** by using

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[1] (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *23*, 1-38. (b) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, 17-38. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103. (d) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479-490. (e) Henrici-Olive, G.; Oive, S. *Angew. Chem.* **1976**, *88*, 144-150; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136-141.

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[4] Nelson, G. O. *Organometallics* **1983**, *2*, 1474.

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[6] See, for instance: Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527-2532.

[7] Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082-4090.

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$[Ph_3PCuH]_6$, a more convenient preparation uses 1 equiv of $NaBH_4$ in THF/H_2O as described by Graham.[5e] Thus after $NaBH_4$ (15 mg, 0.39 mmol) in 1 mL of 1:1 THF/H_2O is allowed to react with $[(\eta\text{-}C_5Me_5)Ru(CO)_2PMe_2Ph]^+[I]^-$ (**2**)[8] (204 mg, 0.37 mmol) in 3 mmol of THF, yellow crystals of **4** (150 mg, 95%) can be isolated.[8] Carefully degassed C_6D_6 solutions of **4** (sealed tube) are stable indefinitely at room temperature. However, at 40 °C, the formyl complex in solution decomposes at varying rates. The following experiment based on the results obtained with complex **3** was undertaken. A C_6D_6 solution of **4** was divided into two NMR tubes—one containing 2 equiv of 9,10-dihydroanthracene and the other one empty—sealed under vacuum and placed in a 40 °C constant-temperature bath. Periodically the samples were removed from the bath and the ^1H NMR spectra recorded. Within 1 h, the sample that did not contain a radical trap had decomposed to a 50:50 mixture of $(\eta\text{-}C_5Me_5)Ru(CO)_2H$ (**5**) and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)H$ (**6**). Within several additional hours of heating, the dicarbonyl hydride **5** in this sample was completely converted to **6**. In stark contrast, the sample containing 9,10-dihydroanthracene decomposed to a 50:50 mixture of **5** and **6** only *after 14 days of heating at 40 °C*. An additional day of heating did not substantially change this ratio.

A possible explanation for the results of decomposition of formyl complexes both in the presence of and in the absence of 9,10-dihydroanthracene is presented in Scheme I. We are, therefore, proposing that the neutral formyl complexes do not decompose by the accepted route, i.e., loss of terminal carbon monoxide followed by deinsertion of the formyl carbonyl, but instead by a pathway initiated by cleavage of the carbon-to-hydrogen bond of the formyl group by miscellaneous radicals. Radical scavengers, such as 9,10-dihydroanthracene, greatly reduce the concentration of such radicals and therefore retard the decomposition of the formyl complexes. Further support for lack of carbon monoxide loss in the initial step is that $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ decomposes only at a temperature greater than 100 °C.[4] Loss of carbon monoxide is presumed to be the first step in this decomposition.[5d] The intermediate **7** formed in the initial hydrogen atom abstraction could be viewed as an acyl radical similar to that commonly proposed in radical-initiated reactions of aldehydes or, alternatively, as a 19-electron ruthenium complex. We believe that once $(\eta\text{-}C_5Me_5)Ru(CO)_2\cdot$ and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)\cdot$ are formed their reaction with **4** is fast, and 9,10-dihydroanthracene does not effectively intercept these 17-electron species until all the formyl complex is decomposed. The decomposition experiment also indicates that reaction of **5** with PMe_2Ph is probably radical initiated since the rate of this substitution slows drastically in the presence of 9,10-dihydroanthracene.

We believe that the data presented here—(1) variable rates of decomposition of the neutral metal formyl complexes **3** and **4** and (2) stabilization of **4** in solution by radical scavengers—indicate that decomposition takes place via a radical chain process involving cleavage of the carbon-to-hydrogen bond of the formyl group in a kinetic step followed by decomposition of the ensuing acyl radical to a more stable ruthenium radical that is the chain carrier. We are continuing to study this and other aspects of carbon monoxide reduction in model ruthenium complexes.

Acknowledgment. We thank the Eastman Chemicals Division for allowing publication of this work.

Registry No. 1, 86853-54-5; **2**, 88296-33-7; **3**, 88296-34-8; **4**, 88296-35-9; **5**, 82728-97-0; **6**, 88296-36-0; $[Ph_3PCuH]_6$, 33636-93-0; DHA, 613-31-0.

Supplementary Material Available: Experimental details for preparation of $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (**2**) and NMR, IR, and analytical data for **2** and **4** (1 page). Ordering information is given on any current masthead page.

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[8] Analytical data for complexes **2** and **4** are satisfactory and are detailed in the supplementary material. An X-ray structure of **4** has been completed: details will be reported later.

Synthesis and Thermal Isomerization of a Cyclobuta[*d*]naphthalenone

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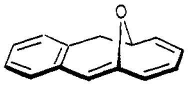
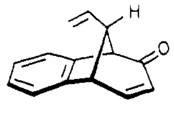
Orbital symmetry constraints serve in an entirely predictable manner to guide many molecules into well-defined thermal and photochemical reaction channels. Effects that may be capable of interfering with this normal kinetic preference have not been systematically investigated, are viewed as subtle, and are not widely appreciated. In the course of another study, we had occasion to prepare the topologically interesting tetracyclic ketone **6**[3] and to examine its thermolysis. An unprecedented, preparatively useful route to benzo fused oxa[10]annulene **7** was uncovered. Of complementary mechanistic significance is the notable involvement of the carbonyl group of **6** in a "symmetry-disallowed" bond reorganization scheme which evidently proceeds at the expense of a Cope rearrangement.

The synthetic protocol (Scheme I) began with selective hydrolysis of diester **1a**[4] (88%) and conversion to crystalline ketone **2** (mp 49–50 °C) by cuprate addition to the acid chloride (88% for two steps).[5] Following ketalization and alteration of the ester oxidation level to give aldehyde **3** (75% overall), the [4.4.4]propellatrienone **4**, mp 55–56 °C, was obtained conventionally (43%). Treatment of **4** with 2 equiv of bromine afforded **5**, which when exposed directly to potassium *tert*-butoxide in dry dimethylformamide (−30 °C, 3 h) furnished **6**, mp 140 °C (55%). The structural assignment to **6**, which was substantiated by X-ray analysis (Figure 1), explicitly defines the striking capacity of enolate anion **5**$^-$ for 1,4-elimination. No five-ring product resulting from 1,5-elimination was detected.

The thermolysis of **6** was most conveniently carried out on packed (Carbowax 20M, SE-30, or QF-1) VPC columns in the 130–175 °C range. Under these conditions, **7** and **8** were efficiently produced in an approximate ratio of 1.1:1.0 and separated chromatographically (7% SE-30 on Chromosorb W, 130 °C). Immediate recourse to X-ray methods showed **7** (mp 96 °C) to be an interesting benzo fused oxa[10]annulene derivative (Figure 2). The structural features of **8** (mp 83 °C) were deduced from its IR and NMR spectra.[6]



7



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The proportion of **7** to **8** remained constant over a wide range of conditions and was invariant to the percent conversion of **6**. A common intermediate is assumed in their formation. While

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[1] Postdoctoral Fellow at the Deutscher Akademischer Austauschdienst (NATO), 1981–1982.

[2] (a) The Ohio State University. (b) Authors to whom inquiries concerning the X-ray analyses should be directed at the University of Houston.

[3] The *Chemical Abstracts* name for this substance is 2,2a-dihydro-2,5a-etheno-5a*H*-cyclobuta[*d*]naphthalen-3(1*H*)-one [Merritt, J., private communication].

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[6] IR (KBr) (cm^{-1}) 3070 (w), 3000 (w), 1677 (s), 1635 (w); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48 (dd, J = 9.6 and 6.9 Hz, 1 H), 7.38 (dd, J = 5.1 and 3.3 Hz, 1 H), 7.25 (m, 1 H), 7.15–7.11 (m, 2 H), 5.66 (ddd, J = 17.2, 10.2, and 7.2 Hz, 1 H), 5.51 (dd, J = 9.6 and 1.6 Hz, 1 H), 5.13 (dt, J = 17.2 and 1.2 Hz, 1 H), 5.02 (dd, J = 10.3 and 1.0 Hz, 1 H), 3.78 (br s), 3.60 (d, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) (ppm) 197.75 (s), 154.54 (d), 146.78 (s), 137.74 (s), 137.55 (d), 127.42 (d), 127.17 (d), 126.51 (d), 124.00 (d), 123.90 (d), 117.28 (t), 64.85 (d), 63.64 (d), 48.95 (d).

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